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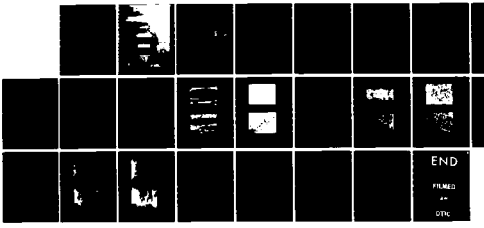

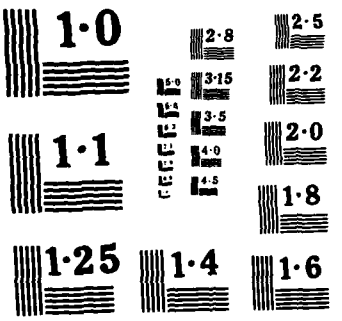

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The objectives of this research program were to investigate the use of a catalyst to increase the char yield of petroleum pitch and thus increase the processing efficiency of carbon-carbon composites, and to investigate the use of an alternate pitch that forms a fine-isotropic matrix microstructure which may improve the interlaminar shear strength of bidirectional carbon-carbon composites. After the first carbonization and heat-treatment cycle, the composite with A240 petroleum-pitch matrix precursor with 20 w/o $AlCl_3$ had a 4 percent higher bulk density. The composite with a fine-isotropic matrix microstructure from a thermal pitch from vacuum-distilled bottoms did not have higher interlaminar shear strength. This matrix was more viscous and did not infiltrate well the fiber bundles through which the shear fracture occurred. Further work is needed to better understand the relationships between char yield, viscosity, and microstructure, and to optimize these properties of the pitch matrix precursors.

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FOREWORD

This is the fourth annual report on a program to study the disclination structures and improved processing of carbon-carbon composites. This work was supported by the Office of Naval Research under Contract N00014-81-C-0641. Dr. L. H. Peebles, Jr. was the scientific officer; his interest and support are gratefully acknowledged.

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INTRODUCTION

The selection of the proper impregnant as the matrix precursor for carbon-carbon composites is a key aspect in the processing science for these composites. The matrix plays a role of shear stress transfer in the mechanical performance of these composites, with the high-strength graphite fibers as the principal tensile and compressive load-bearing constituent. The matrix also plays a major role in the ablation, particle erosion and chemical erosion behavior. In these cases, the microstructure of the matrix -- its graphite-layer orientation and pore structure -- affects the chemical removal of carbon during ablation, rocket-nozzle recession, and oxidation, and contributes to stress wave attenuation and impact resistance during particle erosion.

The matrix impregnant should provide an efficient means for densifying the graphite-fiber preforms; that is, it should have a high carbon yield on carbonization to minimize the number of repeated impregnations and carbonizations needed to achieve the required composite density. The matrix precursors currently in use are Allied 15V coal-tar pitch, Ashland 240 petroleum pitch, and phenolic resin. Neither was selected to afford an optimum precursor and matrix microstructure. Their use stems from polycrystalline graphite fabrication, or from ablative phenolic heatshields, where their role was different from their new role in carbon-carbon composites.

The objective of this research program was to investigate the use of alternate impregnants for carbon-carbon composites in order to develop a matrix precursor that ensures efficient densification and provides an appropriate matrix microstructure. Specifically, this program investigated the use of a catalyst to increase the char yield of petroleum pitch and thus increase the processing efficiency of carbon-carbon composites, and the use of an alternate pitch that forms a fine-isotropic matrix microstructure which may improve the interlaminar shear strength of bidirectional carbon-carbon composites.

BACKGROUND

Catalysts

The carbonization of organic pitches to form the carbonaceous mesophase is a complex chemical process that involves thermal cracking and condensation, or polymerization, reactions. The pitches from petroleum and coal tar are comprised of relatively small aromatic molecules with aliphatic side chains. These molecules are a flat array of fused benzene rings with linear carbon chains attached to the edges of the disk. The average molecular weight is about 400. The first step in carbonization is to thermally crack off the larger aliphatic chains. The disklike molecules then polymerize to form larger disklike molecules. The carbonaceous mesophase, a discotic nematic liquid crystal, then forms from these larger molecules with a molecular weight of about 1500.

The thermal condensation reactions to form the carbonaceous mesophase occur by a radical mechanism and by the Friedel-Crafts reaction. These condensation reactions can be influenced by catalysts. In radical pyrocondensation, the radicals that are capable of condensation are formed during the degradation or thermal cracking reactions. The Friedel-Crafts reaction involves attaching alkyl side chains to aromatic rings. In aromatic condensation, the attached alkyl chain contributes to ring closure to complete the fused benzene ring structure. This reaction is generally carried out in the presence of Lewis acids, such as aluminum chloride ($AlCl_3$), BF_3, HF, $SnCl_4$, or phosphoric acid.

Extensive work has been done by Mochida, et al.,[1,2] on the carbonization of aromatic hydrocarbons in the presence of catalysts. This work was aimed primarily at producing a better needle coke for electrode graphites. The carbonization of the pure aromatic hydrocarbons, napthalene, anthracene, chrysene, and phenanthrene, in the presence of 0.1 mol fraction $AlCl_3$, resulted in benzene insoluble contents at 380°C of 98, 88, 82, and 69 percent, respectively. The effect of the amount of catalyst on the carbonization of chrysene is shown in Figure 1. The catalyst accelerates the carbonization in proportion to the amount of $AlCl_3$ up to 0.1 mol fraction. Here, BI (benzene insolubles) is a measure of the amount of mesophase present. The addition of the catalyst results in a greater amount of mesophase that forms at a given temperature; that is, the catalyst accelerates the rate of carbonization. Other Lewis acids such as ferric or cupric chloride did not work as catalysts for the carbonization of these aromatic hydrocarbons. Mochida[2] also showed that alkali metals catalyze the carbonization of these pure aromatic molecules, as shown in Figure 2.

Not only can catalysts increase the rate of mesophase formation and increase carbon yield, but they can alter the microstructure of the carbonized coke. In the catalytic carbonization of napthalene and anthracene with the alkali metals lithium, sodium, and potassium,[2] the resulting carbonized coke was an isotropic coke as compared to an uncatalyzed, anisotropic needle coke. The isotropic coke was similar to glassy carbon with respect to crystallite size, surface area, and specific gravity.

The implication of this work on the carbonization of petroleum pitches may be that those molecules that are normally lost as volatiles and those that are not in the proper reactive state can be forced to condense by the catalytic reactions and thus contribute to the carbon yield of the pitch. Carbonization

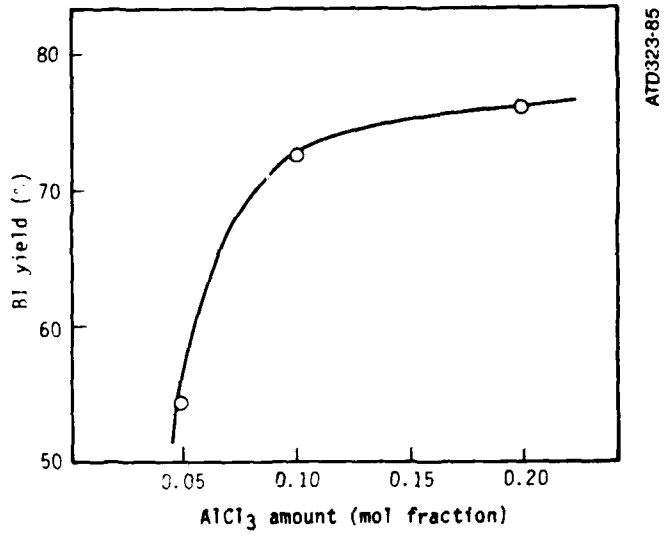


Figure 1. Influence of the amount of $AlCl_3$ catalyst on the carbonization yield of chrysene; 2 hr at 380°C

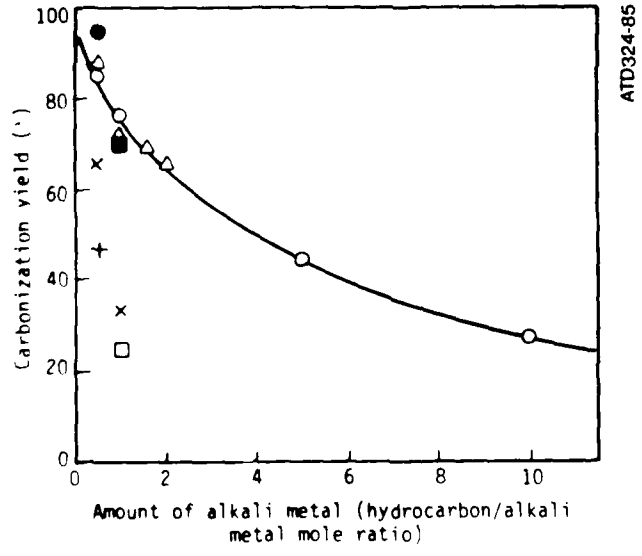


Figure 2. Carbonization yield of aromatic hydrocarbons versus amount of alkali metal; heat-treatment, 2 hr at 500°C. +, Anthracene + Li; x, Anthracene + Na; ○, Anthracene + K; ●, Anthracene + K (in Diglyme); △, Pyrene + K; □, Naphthalene + K; ■, Naphthalene + K

may be conducted at lower temperatures or at lower pressures. The use, then, of catalysts in the carbonization of pitches for the matrix of carbon-carbon composites should result in higher carbon yields, a more efficient mesophase transformation, and a means for altering the matrix microstructure.

Alternate Precursors

Petroleum pitch is derived from the more aromatic refinery streams from which the asphaltene components have been removed by cracking and distillation. The microstructure of pyrolyzed petroleum pitch is characterized as an acicular or fine fibrous microstructure which results from the deformation by bubble percoation of a mesophase of rather low viscosity.

The other major type of microstructure is the fine-isotropic microstructure typical of Gilsonite coke and cokes from reduced crudes and asphalts. Their precursors tend to have a higher content of aliphatic chains attached to the aromatic molecules. The fine-isotropic structure is produced by the coalescence of mesophase spherules with a higher viscosity which does not permit structural rearrangement or deformation. The isotropic microstructure can be visualized as a piece of paper wadded in a ball. Here the paper represents the orientation of the stacks of parallel disklike molecules and their three-dimensional intertwining. The needle structure can be visualized as a series of curtains with all the molecules oriented in the plane of the curtains. The layers are corrugated about the needle axis along the length of the curtains.

The use of a precursor that forms a fine-isotropic microstructure for carbon-carbon composites has several promising attributes. These include higher carbon yield, increased strength and toughness, and higher viscosity. The higher viscosity may help volumetric yield; that is, the mesophase may not be as easily forced out of the composite by the pressure of trapped volatiles.

On the other hand, the higher viscosity may hinder effective infiltration into small pores. The isotropic cokes tend to have higher thermal expansions. Polycrystalline graphites have been fabricated from a variety of cokes,[3] and the properties of these graphites provide insight on the nature of these isotropic coke-forming precursors as matrix materials. The strength of isotropic-coke graphites is generally much higher than that for needle-coke graphites, as illustrated in Figure 3. There is an easy cleavage path in needle coke, parallel to the corrugated layers (curtains). But in an isotropic coke, cleavage is difficult and not easily propagated through the isotropic structure (wadded paper ball).

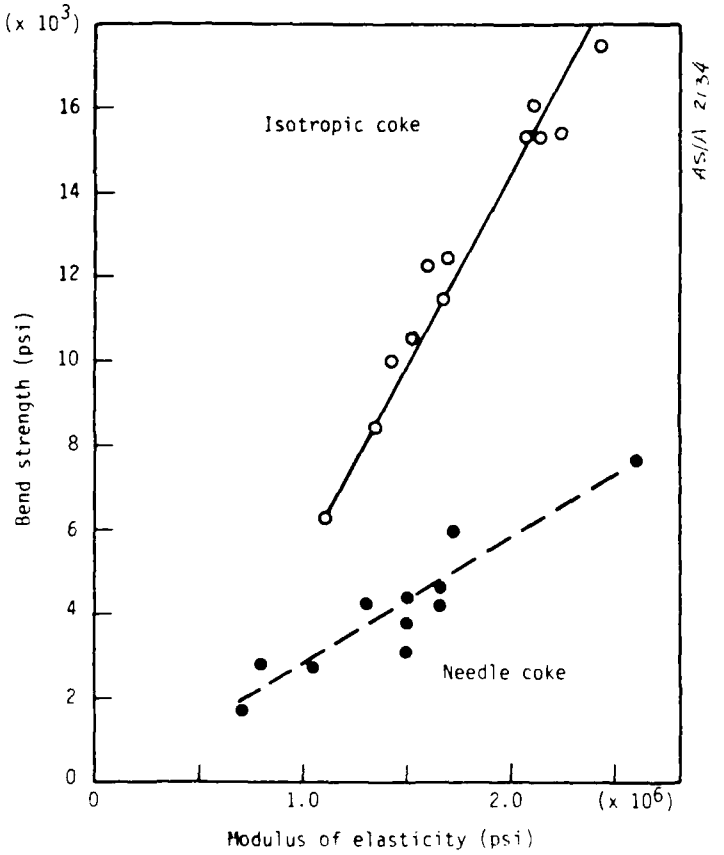


Figure 3. Strength and modulus of polycrystalline graphites fabricated from isotropic and needle cokes

EXPERIMENTAL RESULTS

Catalysts

The char yields of A240 petroleum pitch with various amounts of $AlCl_3$ catalyst are shown in Figure 4. One-gram samples were heated at 20°C/hr to 600°C. Included in the char yield value is the residual amount of $AlCl_3$. The char yield for the pitch alone, however, is significantly increased due to the presence of the catalyst. The maximum char yield occurred with 20 w/o $AlCl_3$, which is about 0.4 mol fraction. The effect of the catalyst on the char yield of two other pitches is shown in Figure 5. For the thermally treated pitch (20 hr at 380°C), most of the lower molecular-weight molecules were removed by volatilization. The addition of the catalyst increased the yield slightly, indicating that the role of the catalyst in the untreated pitch is to prevent these low molecular-weight molecules from volatilizing by promoting condensation and polymerization.

Bidirectional composites were fabricated with the catalyzed pitch precursor to determine the increase in densification efficiency with the high char-yield material. The composites were fabricated by combining plies of an eight-harness satin fabric of heat-treated T300 fibers with the ground pitch-catalyst mixture (20 w/o $AlCl_3$) in a punch and die mold. The layup was carbonized to 500°C and pressed to stops at 400°C to obtain 60 v/o fibers. After carbonization, the composite panels (5 cm × 5 cm × 0.7 cm) were heat treated to 1500°C.

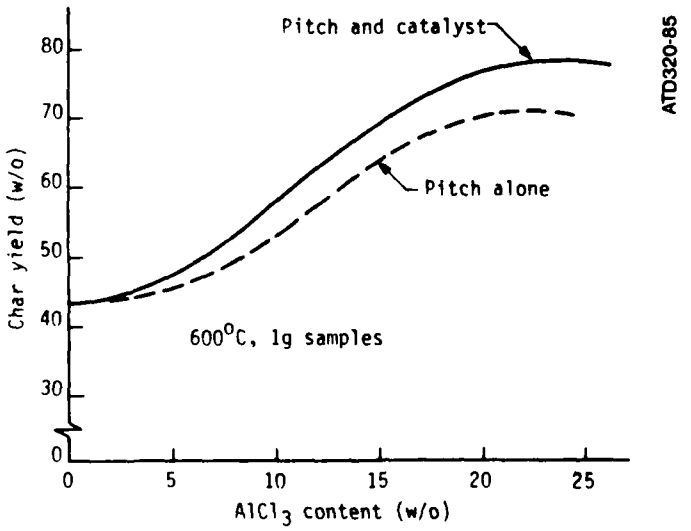


Figure 4. Effect of catalyst on char yield of A240 petroleum pitch

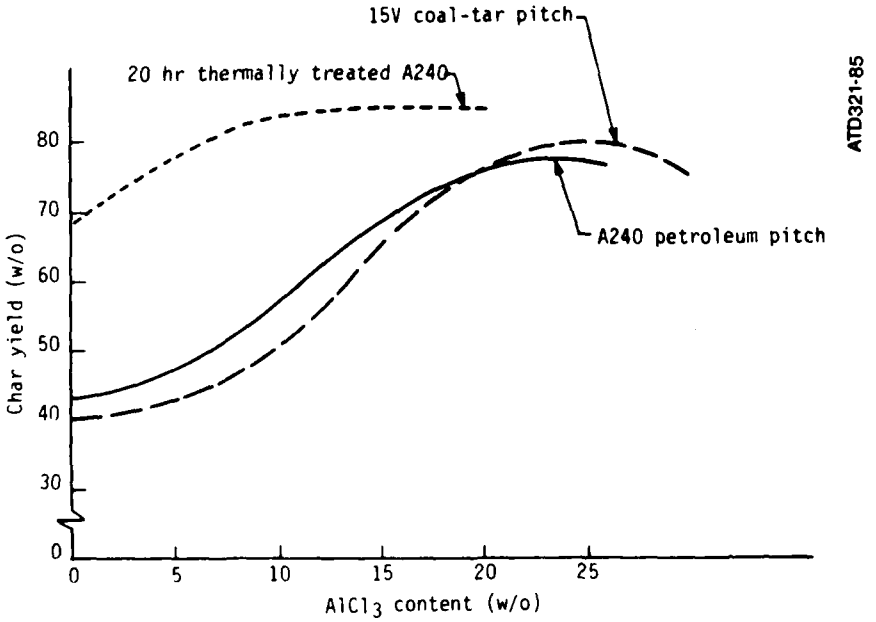


Figure 5. Effect of catalyst on char yield of other pitches

The bulk densities of the composite panels are shown in Figure 6 for the different process steps and for the catalyzed and uncatalyzed pitch precursor. The higher density after carbonization for the catalyzed composite reflects both the increased char yield and the retained $AlCl_3$. The 1500°C heat treatment removed all the $AlCl_3$. The resulting 4 percent increase in composite density reflects a 10 percent increase in the total matrix density (60 v/o of the composite is fibers). The matrix is porous, thus the density increase for the composite matrix is about 20 percent and is similar to that for the pitch itself (Figure 4). These data indicate that processing efficiency can be improved with the use of catalysts in the pitch-matrix precursor.

Optical micrography (Figures 7 and 8) of the bidirectional composites with and without catalyst showed that the microstructure of the catalyzed matrix had more of a fine-isotropic structure than a fibrous structure. Also,

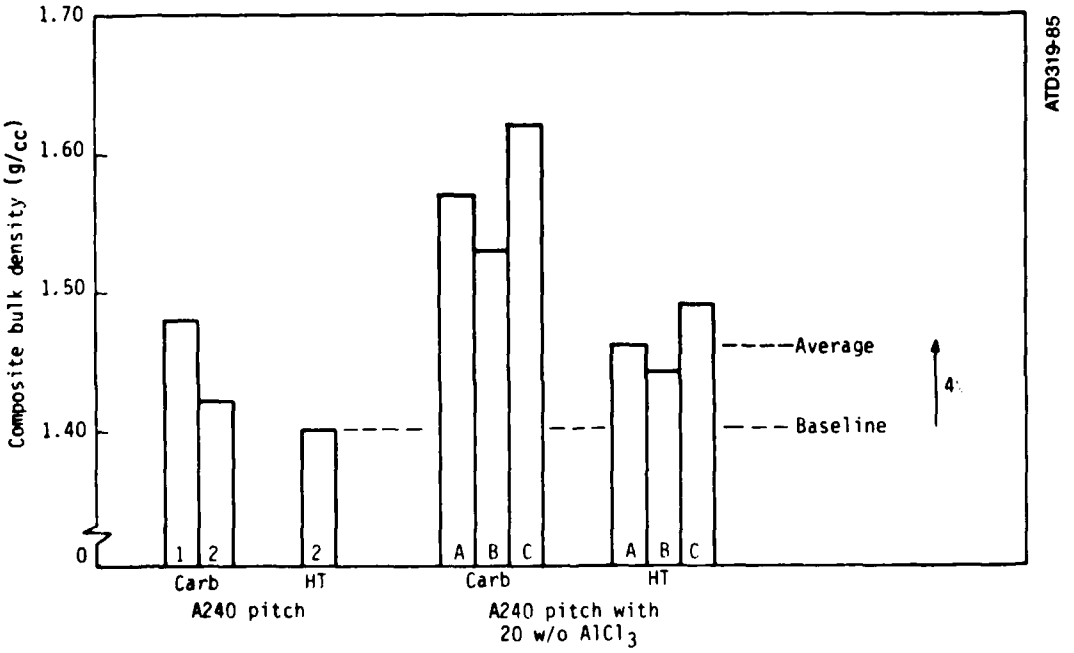


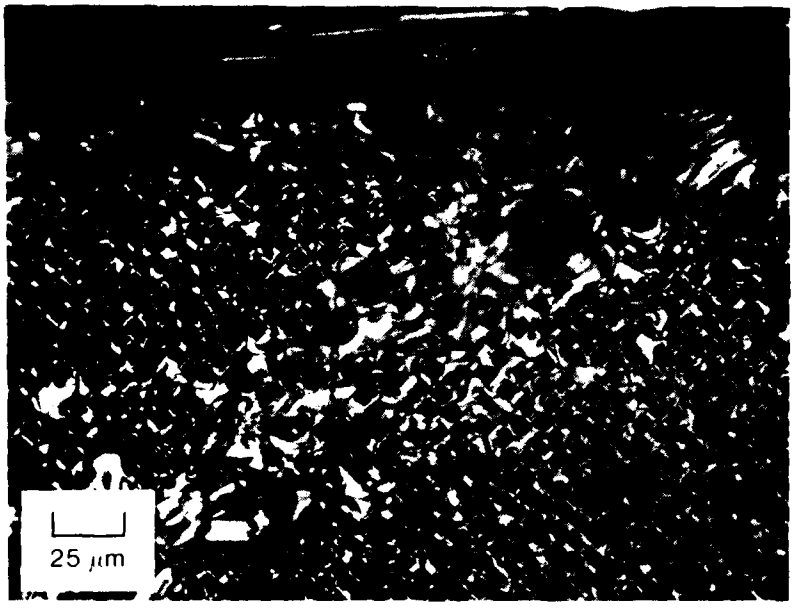
Figure 6. Bulk density of composites with pitch-catalyst matrix precursor

A240 pitch matrix

A240 pitch with $AlCl_3$ matrix

Figure 7. Optical micrographs of bidirectional composites showing better filling of matrix areas with catalyzed pitch

A240 pitch matrix



A240 pitch with $AlCl_3$

Figure 8. Optical micrographs of matrix in composite; matrix structure inside fiber bundles is similar

the matrix tended to better fill the spaces between fabric plies, suggesting that the mesophase from the pitch-catalyst mixture had a higher viscosity. The catalyst was removed from the matrix by the heat treatment without a significant change in the microstructure (Figure 9).

Alternate Pitch Precursor

A thermal pitch from vacuum-distilled bottoms was obtained from Mobil Research and Development Corporation. The as-received pitch had a char yield of 19 percent and was heat treated for 12 hr at 385°C to increase the char yield to 51 percent. The microstructure of the carbonized thermal pitch was fine isotropic (Figure 10). Bidirectional composite panels were fabricated in the same manner as for the catalyst composites. These panels were designed to provide test specimens for measurement of interlaminar shear strength. The ground pitch was sprinkled between the fabric plies and the layup was carbonized to 500°C. The panel and mold were pressed to stops to obtain 60 v/o fibers. After a heat treatment to 1500°C, the panels were vacuum impregnated with the as-received pitch to increase the composite density. Carbonization and a 1500°C heat treatment followed the impregnation. The bulk density of the composite panels with the thermal-pitch matrix and A240-pitch matrix are given in Table 1. Shear strength was measured with a double-notched specimen loaded in compression (Figure 11).

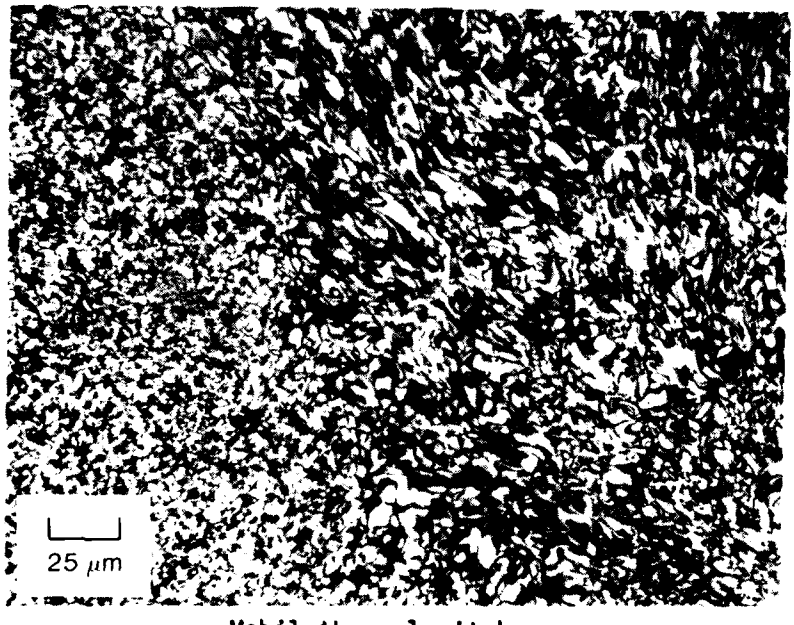
Optical micrography (Figures 12 and 13) of the composite with the alternate thermal pitch showed that the matrix had a fine-isotropic microstructure. The matrix filled the spaces between fabric plies better than the A240-pitch matrix, whereas the thermal-pitch matrix did not fill the individual fiber bundles well. This indicates that the mesophase from the thermal pitch had a higher viscosity. Also, on heat treatment, the thermal-pitch matrix exhibited wider, more pronounced shrinkage cracks

Carbonized

Heat treated to 1500°C

Figure 9. Effect of heat treatment on composite with catalyzed matrix

A240 petroleum pitch



Mobil thermal pitch

Figure 10. Optical micrographs of carbonized pitches; fine-isotropic structure of alternate pitch; coarse, deformed structure of more fluid petroleum pitch

Table 1. Density of bidirectional composite with alternate precursor

Composite	Bulk Density (g/cc)	
	First Heat Treatment	Second Heat Treatment
A240 pitch	1.40	1.61
Mobil thermal pitch	1.39	1.57

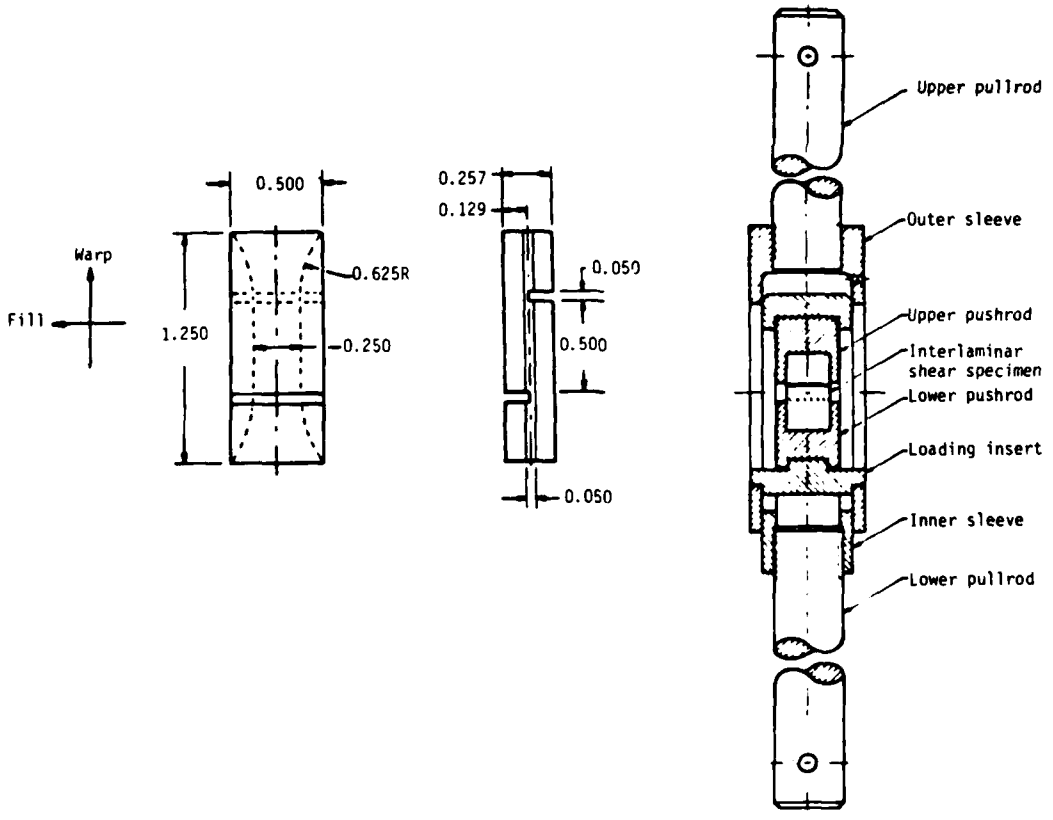
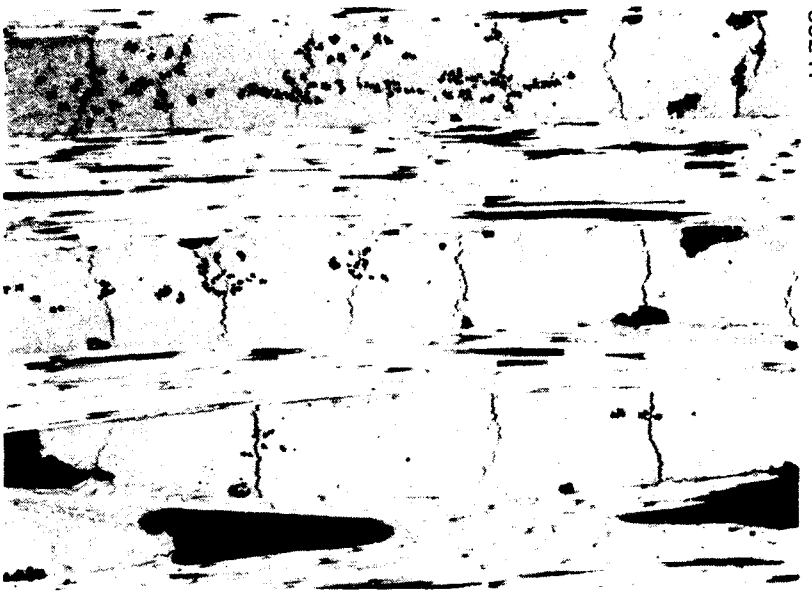
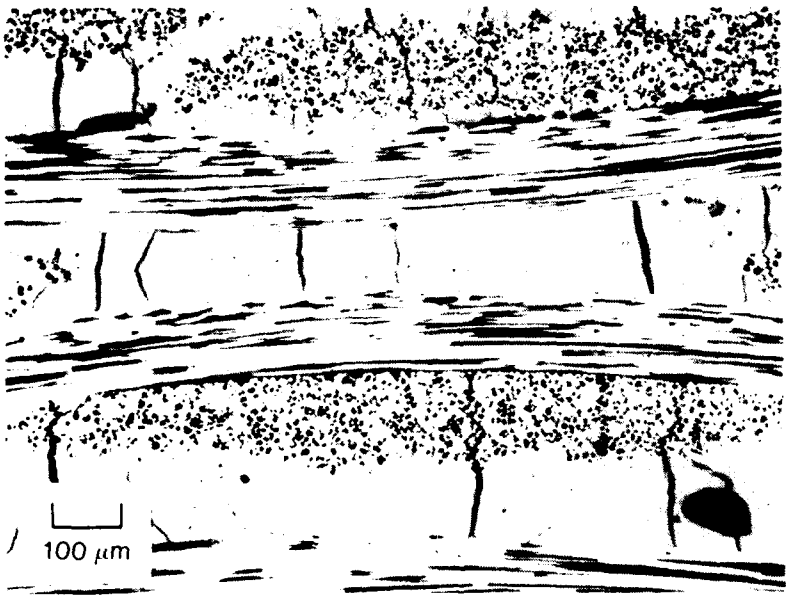


Figure 11. Double-notched shear test for interlaminar shear strength

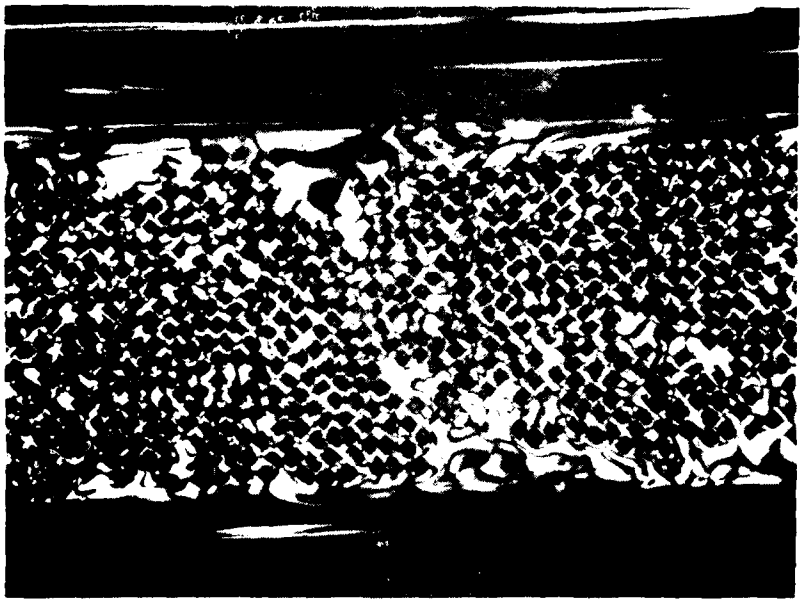


A240 pitch



Mobil thermal pitch

Figure 12. Optical micrographs of bidirectional composites with petroleum and thermal pitch precursors



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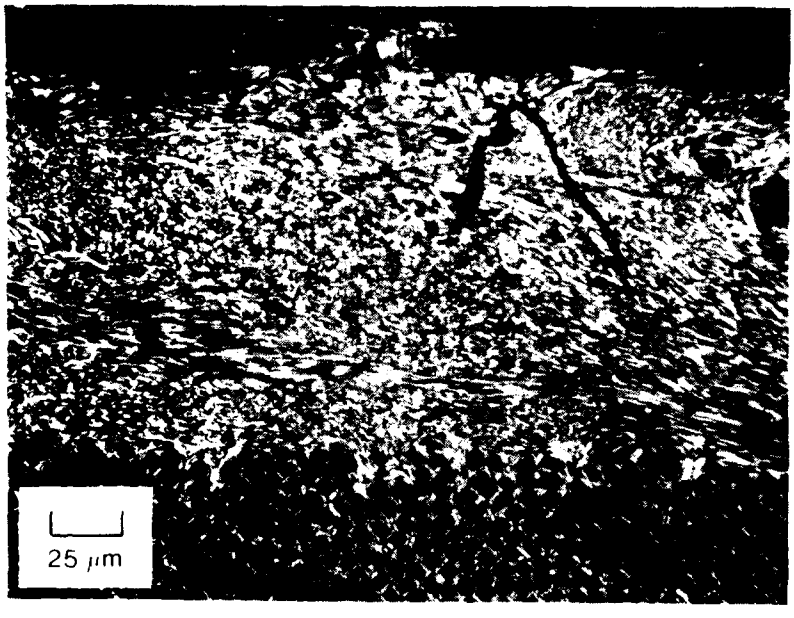
A240 pitch

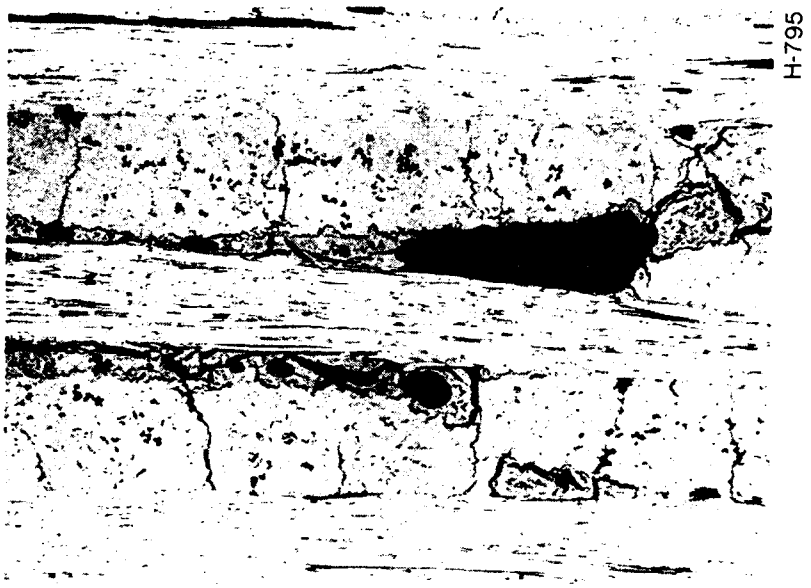


Mobil thermal pitch

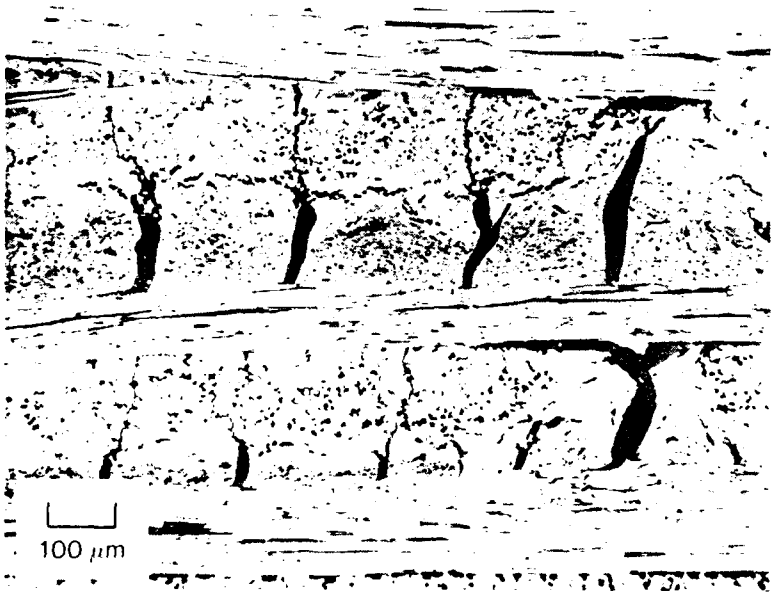
Figure 13. Optical micrographs of bidirectional composites; more fluid petroleum pitch better fills fiber bundles; more viscous alternate pitch fills gaps between fabric plies

(Figures 14 and 15), indicating that the fine-isotropic microstructure has a higher expansion (and shrinkage) than the fibrous microstructure of A240-pitch mesophase.

The interlaminar shear strengths of the composite panels are shown in Figure 16. The lower (unexpected) shear strengths for the composite with the fine-isotropic matrix may be attributed to its shrinkage and viscosity characteristics. Observation of the fractured surfaces of the shear specimens (Figures 17 and 18) showed that the thermal-pitch composites failed on a plane that traversed through the individual fiber bundles. The A240-pitch composites failed between plies. The fiber bundles of the thermal-pitch composite were not well impregnated, due to the higher viscosity of the thermal-pitch mesophase. The shrinkage cracking in the fine-isotropic matrix may have provided a weakened structure.

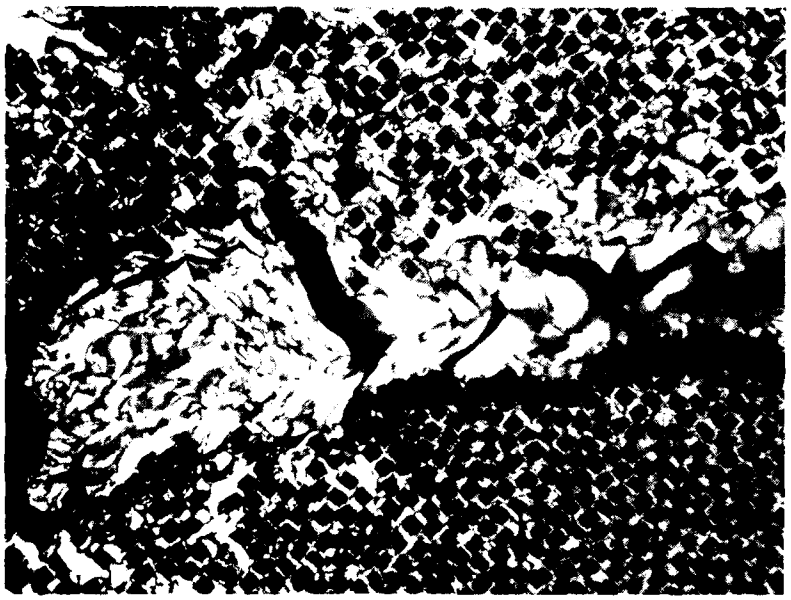


A240 pitch

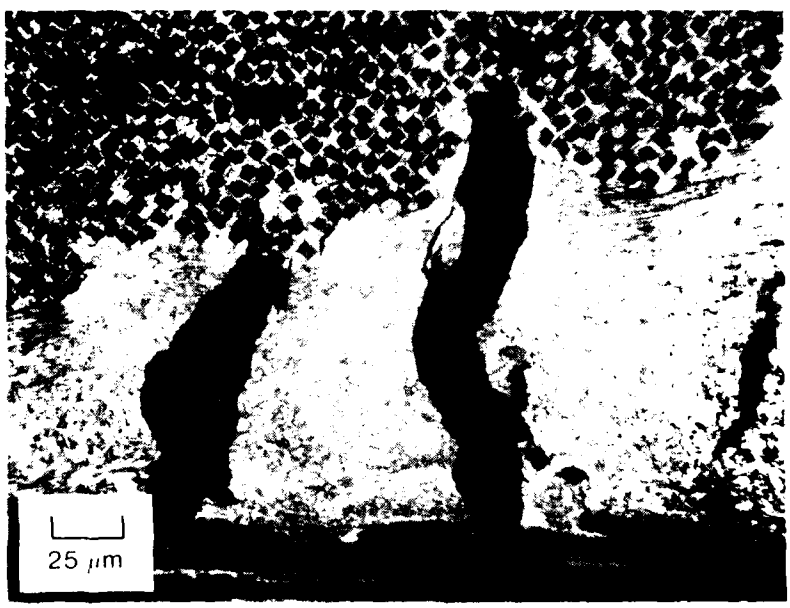


Mobil thermal pitch

Figure 14. Shrinkage cracks in matrix of bidirectional composites



A240 pitch



Thermal pitch

Figure 15. Shrinkage cracks in matrix; fine-isotropic matrix, with greater shrinkage, had wider shrinkage cracks; cracks did not follow layer orientation as well as in petroleum-pitch matrix.

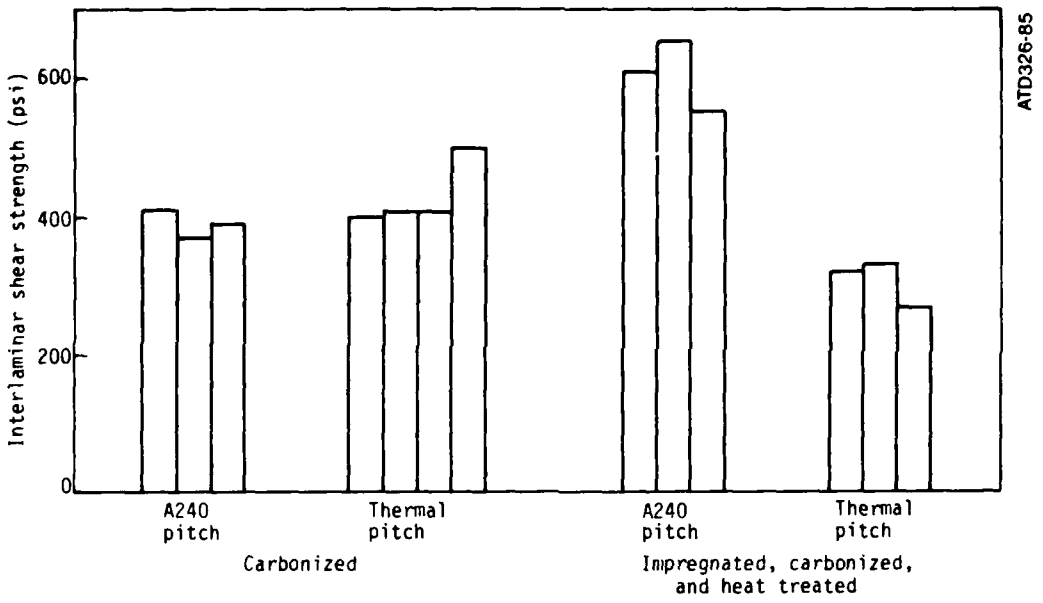
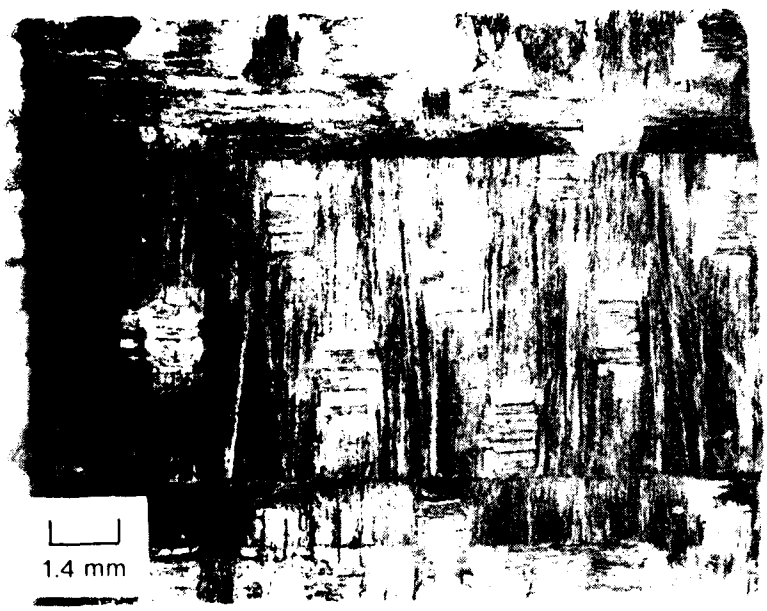


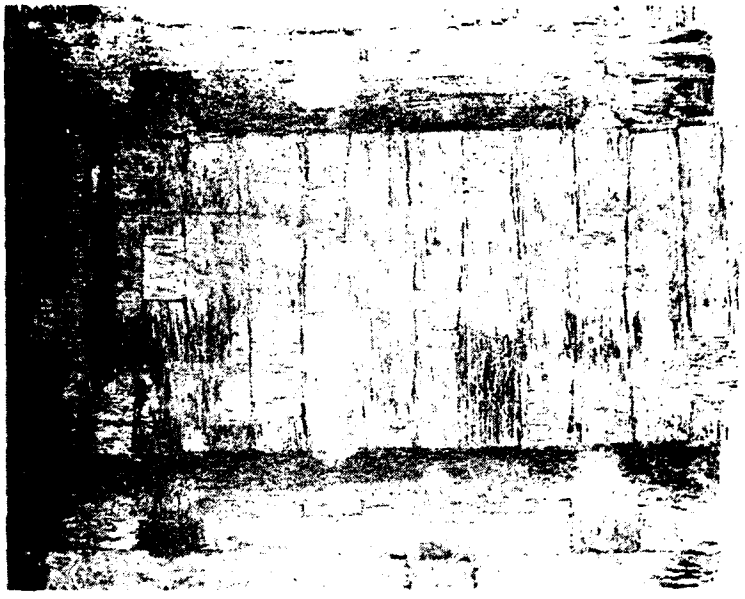
Figure 16. Interlaminar shear strength of composite with fine-isotropic matrix microstructure

A240 pitch



Thermal pitch

Figure 17. Macrographs of fracture surface of double-notched shear specimens of carbonized composites



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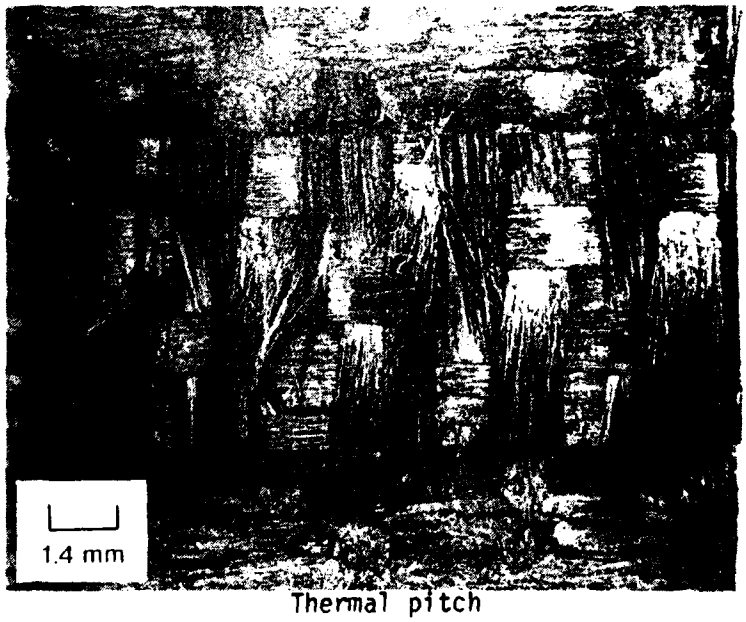
A240 pitch



Thermal pitch

Figure 18. Macrographs of fracture surface of double-notched shear specimens of heat-treated composites

SUMMARY

The use of the catalyst, $AlCl_3$, significantly increased the char yield of A240 petroleum pitch. This increase in matrix yield resulted in an increase in the bulk density of a bidirectional carbon-carbon composite fabricated with a catalyst content of 20 w/o in the petroleum pitch. Heat treatment to 1500°C removed the residual catalyst. The heat-treated composite had a 4 percent higher bulk density after the first cycle than the composite without the catalyst-pitch mixture. The catalyzed pitch matrix better filled the gaps between fabric plies. This work has shown that the process efficiency can be improved with the use of the catalyst for bidirectional composites with pitch precursors.

The alternate pitch precursor had a fine-isotropic microstructure after carbonization. In the carbon-carbon composite, the matrix filled the gaps between the fabric plies well, but not the fiber bundles. This indicates that the mesophase from this alternate pitch had a higher viscosity. The interlaminar shear strength was not significantly higher for the composite with the alternate pitch matrix; the failure path was through the porous fiber bundles. Adjustment of the viscosity of this thermal pitch by reducing the initial thermal treatment should produce a pitch which would better fill the fiber bundles and still provide the fine-isotropic matrix microstructure.

This work suggests that the key properties of a pitch precursor for the matrix of a bidirectional carbon-carbon composite are char yield, viscosity,

and microstructure. A high char yield increases densification efficiency, but viscosity also increases with char yield. The viscosity should be low enough to wet and impregnate the tightly packed filaments in a fiber bundle, but high enough to retain the mesophase in the larger spaces between fabric plies. A fine-isotropic microstructure has higher toughness, but also higher expansion which contributes to shrinkage cracking. Thus, further work is needed to better understand the relationships between char yield, viscosity, and microstructure, and to optimize these properties of the pitch-matrix precursors.

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PUBLICATIONS

The following technical publications have been prepared with support in part by this research program:

1. J. E. Zimmer, and J. L. White, Advances in Crystals 5 (1982) 157. A review article entitled "Disclination Structures in the Carbonaceous Mesophase."

2. J. E. Zimmer and J. L. White, Carbon 21 (1983) 323. A letter to the editor entitled "Mesophase Alignment Within Carbon-Fiber Bundles."

3. J. E. Zimmer, "Disclinations and Fracture," presentation at International Symposium on Carbon, November 1-4, 1982, Toyohashi, Japan.

4. J. E. Zimmer and R. L. Weitz, Extended Abstracts, 16th Conference on Carbon, (1983) p. 92. A paper entitled "Disclinations in a Graphite-Fiber Bundle."

5. J. E. Zimmer and R. L. Weitz, Extended Abstracts, Carbon 84, International Carbon Conference, Bordeaux, France (July, 1984), 386. A paper entitled, "Three-Dimensional Disclination Arrays."

6. J. E. Zimmer and R. L. Weitz, Extended Abstracts, 17th Conference on Carbon, (1985) 396. A paper entitled "Magnetic Field Alignment of Carbon Composite Matrix."

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